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Evaporation from Nanopores: Probing Interfacial Transport

by

Zhengmao Lu

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Abstract

Evaporation, a commonly found phenomenon in nature, is widely used in thermal management, water purification, and steam generation as it takes advantage of the enthalpy of vaporization. Despite being extensively studied for decades, the fundamental understanding of evaporation, which is necessary for making full use of evaporation, remains limited up to date.

It is in general difficult to experimentally characterize the interfacial heat and mass transfer during evaporation. In this thesis, we designed and microfabricated an ultrathin nanoporous membrane as an experimental platform to overcome some critical challenges including: (1) realizing accurate and yet non-invasive interface temperature measurement; (2) decoupling the interfacial transport resistance from the thermofluidic resistance in the liquid phase and the diffusion resistance in the vapor phase; and (3) mitigating the blockage risk of the liquid-vapor interface due to non-evaporative contaminants. Our nano device consisted of an ultrathin free-standing membrane (~200 nm thick) containing an array of nanopores (pore diameter ~100 nm). A gold layer deposited on the membrane served as an electric heater to induce evaporation as well as a resistive temperature detector to closely monitor the interface temperature. This configuration minimizes the thermofluidic resistance in the liquid and mitigates the contamination risk.

We characterized evaporation from this nano device in air as well as pure vapor. We demonstrated interfacial heat fluxes of ~500 W/cm² for evaporation in air, where we elucidated that the Maxwell-Stefan equation governed the overall transport instead of Fick’s law, especially in the high flux regime. In vapor, we achieved kinetically limited evaporation with an interfacial heat transfer coefficient up to 54 kW/cm² K. We utilized the kinetic theory with the Boltzmann transport equation to model the evaporative transport. With both experiments and modeling, we demonstrated that the kinetic limit of evaporation is determined by the pressure ratio between the vapor in the far field and that generated by the interface. The improved fundamental understanding of evaporation that we gained indicates the significant promise of utilizing an ultrathin nanoporous design to achieve high heat fluxes for evaporation in thermal management, desalination, steam generation, and beyond.

Thesis Supervisor: Evelyn N. Wang

Title: Gail E. Kendall Professor of Mechanical Engineering
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1. Introduction

1.1 Background

Evaporation is an effective cooling mechanism commonly found in nature and widely used in thermal management of electronics [1-7] as it takes advantage of the enthalpy of vaporization. Even for cooling solutions such as pool boiling [8-12] and flow boiling [13-18], it is still evaporation that governs the transport process at the interface level. In water desalination [19, 20] and steam generation [21-23], evaporation also plays an important role. It was reported in 2013 that thermal process (using evaporation) represented around 70% market share in desalination industry in Gulf cooperation council countries [24].

Despite being extensively used and investigated for decades, the understanding of evaporation remains limited at the fundamental level. Pauken characterized water evaporation from a heated pool dominated by free and forced convection where the temperature of water was only measured in the bulk [25]. Gang and Ward measured the temperature profile across the interface of an evaporating liquid in a glass funnel with thermocouples positioned by microstages [26]. However, the temperature gradient along the interface was unclear and whether the thermocouple in the way of the vapor flow disturbed evaporation locally was questionable. Saylor et al. probed the temperature field for water surface undergoing evaporation with an infrared camera although the heat fluxes were rather low (0.03 to 0.5 W/cm²) [27]. Smith et al. applied Raman thermometry to test the cooling rates for transient evaporation of a droplet train of liquid water injected into vacuum [28]. Their heat transfer model, however, failed to accounted for the size change of the droplet and the associated enthalpy change as a function of time. The droplet was divided into 100, 65 nm thick spherical shells and each cell was considered to be isothermal, but the choice of the
cell thickness was somewhat arbitrary, to which the results were quite sensitive based on the analysis in the paper.

Proper theoretical treatment of evaporation is also a topic still under significant discussion. In his thesis in 1954 [29], Schrage proposed a modeling framework for transport across the interface with vapor in contact with its own condense phase. He pointed out that there must be a net mass flux across the interface and at some distance from the interface, the deviation from the Maxwell-Boltzmann equation must be relatively small. At that location, the molar moving towards the interface (-z direction) \( w_{\infty} \) can be written as:

\[
 w_{\infty} = \int_{u_z < 0} f_u u_z du
\]

where \( u \) is the molecular velocity and \( u_z \) is its z-component and

\[
 f_u = n_{\infty} \frac{\exp\left[-\left(u - u_{\infty}\right)^2 / 2RT_{\infty}\right]}{(2\pi RT_{\infty})^{3/2}}
\]

where \( n_{\infty}, u_{\infty}, \) and \( T_{\infty} \) are the vapor number density, bulk velocity and temperature in the far field, respectively, and \( R \) is the specific gas constant. Schrage assumed that these molecules would all arrive at the interface and condense with a probability \( \sigma_c \). Therefore the net flux \( w \) in the system can be expressed as

\[
 w = \sigma_c w_{s+} - \sigma_c w_{s-} = n_{\infty} u_{\infty}
\]

The second equality comes from evaluating the molar flux in the far field. Here, \( \sigma_c \) is the so-called evaporation coefficient [28] and \( w_{s+} \) is the molar flux from integrating the positive half of the Maxwell-Boltzmann equation:
where \( n_s \) and \( T_s \) are the equilibrium vapor number density and temperature the interface, respectively. When the interfacial heat flux is small and \( \sigma_c = \sigma_e = \sigma \), applying the ideal gas law, eq. (1.3) can give the mass flux across the interface in an explicit form:

\[
j = \frac{2\sigma}{2 - \sigma} \frac{1}{\sqrt{2\pi R T_s}} \left( \frac{P_s}{\sqrt{RT_s}} - \frac{P_e}{\sqrt{RT_e}} \right)
\]  

(1.5)

where \( P_s \) and \( P_e \) are the pressure of the equilibrium vapor at the interface and in the far field, respectively. Equation (1.5) is the most commonly used form for evaporative heat transfer [30-32]. However, a key drawback here is that it violates the momentum balance and energy conservation to assume all molecules considered in eq. (1.1) end up striking onto the interface [33]. Even though recent molecular dynamics simulations claimed to have validated Schrage’s approach, it is possible that the simulation domain was too small so that the collisions between vapor molecules was not properly accounted for which on the hand coincided with the assumption made in Schrage’s derivation [34, 35].

To properly account for mass conservation, momentum balance, and energy conservation, the Boltzmann transport equation (BTE) was considered for the evaporation problem. Ytrehus [36] obtained a moment solution of BTE assuming Euler equilibrium in the far field and half Maxwell-Boltzmann molecular emission at the interface, essentially the same boundary conditions as described in [29]. Meland et al. extended the solutions for non-unity evaporation and condensation coefficients [37]. Frezzotti solved the BTE with direct simulation Monte Carlo method [38] and showed that the type of kinetic equation or intermolecular potential has very little influence on the
evaporative flux given a working condition, except that polyatomic molecules behave very
differently from monoatomic ones.

Although the BTE give a consistent description of the vapor molecule motions, it cannot resolve
the exact values of evaporation and condensation coefficients. Instead, they have to be prescribed
as the boundary conditions for the BTE simulation. Molecular dynamics were used to characterize
$\sigma_e$ and $\sigma_c$. Tsuruta et al. simulated evaporation for argon [39] and water [40] and found the
condensation coefficient primarily depended on the translational energy and the surface
temperature. It increases with the former and decreases with the latter. On the other hand, Yang et
al. [41] studied evaporation of a thin layer of water and claimed that the hydrogen bond might
reduce the evaporation coefficient and reported in general lower values and an opposite trend with
interface temperature. Ishiyama et al. evaluated evaporation from liquid into a virtual vacuum with
molecular dynamics for water and methanol [42]. They concluded that the evaporation coefficients
of water and methanol increase and approach unity with decreasing temperatures. Meland et al.
simulated a much larger domain for evaporation including the far field equilibrium vapor for a
Lennard-Jones fluid. They reported even under small non-equilibrium the evaporation coefficient
can be different from the condensation coefficient.

Clearly, there has not been a consensus for the appropriated theoretical description of evaporation
at the interface level. Other attempts include the statistical rate theory [43] and non-equilibrium
thermodynamics, which also drew some contradicting conclusions. Nevertheless, it motivates this
thesis, the goal of which is to address the experimental challenges and improve the fundamental
understanding of evaporation.
1.2 Overall Concept

We identified several experimental challenges for characterizing the interfacial transport which include: (1) measuring the interface temperature accurately and non-invasively; (2) decoupling the interfacial thermal resistance from the thermofluidic resistance in the liquid phase and the diffusion resistance in the vapor phase; and (3) mitigating the risk of blockage of evaporating surface due non-evaporative contaminants.

The uncertainty in temperature measurement $\delta T$ can be estimated as

$$\delta T = \frac{q'' \Delta L}{k}$$  \hspace{1cm} (1.6)

where $q''$ is the interfacial heat flux, $k$ is the thermal conductivity of the working fluid, and $\Delta L$ is the uncertainty in where the temperature measurement is taken. When $q''$ becomes higher, $\delta T$ also increases. When $q'' = 100$ W/cm$^2$ and $k = 0.6$ W/m-K (for water), we obtain that $\Delta L < 3$ $\mu$m is necessary for $\delta T < 5$ °C, which has been difficult to achieve in previous work [25, 27, 44-47]. It is also necessary to minimize the transport resistance associated with the heat supply and liquid refilling. Otherwise, it is not possible to reach a high flux across the interface. For example, Xiao et al. proposed a nanoporous configuration [4] for evaporation studies, where $\Delta L$ was reduced to the pore radius ($\approx$ 75 nm), but their evaporative flux was still limited by the viscous loss in the refilling liquid flow along the pore due to the large pore length (>50 $\mu$m). In addition, the evaporation rate is very sensitive to contamination in the system. If the contaminants do not evaporate, the liquid-vapor interface accumulates the contaminants and eventually clogs the pores.

To address these issues, we designed and fabricated an ultrathin nanoporous membrane device. Figure 1-1 shows the nanodevice design that allows the liquid to wick into the nanopores in the membrane with capillarity, where it is resistively heated by a metal layer and evaporates. The
membrane thickness is designed to be \( t_m \sim 200 \) nm and the pore diameter is \( d_p \sim 100 \) nm. The combination of small \( d_p \) and \( t_m \) minimizes the thermal resistance (\( \sim d_p \)) and viscous loss (\( \sim t_m \)) in the liquid phase and we need a large number of pores to ensure high signal (evaporation) to noise (heat loss) ratios during the experiment. Note that the metal layer can also serve as a resistive temperature detector (RTD) which monitors the interface temperature in close vicinity in an accurately and yet non-invasive manner.

\[ \frac{dc}{dz} + v_m c = 0 \]  
\[ (1.7) \]

Figure 1-1 Schematic of evaporation from a nanopore (not to scale). The top metal layer is resistively heated to induce evaporation from a pinned meniscus in each nanopore and also serves as a resistive temperature detector.

The ultrathin membrane mitigates the clogging risk which nanoporous configurations are often prone to. The mass fraction of non-evaporative contaminants in the nanopore \( c(z) \) is governed by the 1-D steady state diffusion convection equation:
where $D_c$ is the diffusion coefficient of the contaminant in liquid water ($\sim 10^{-5}$ cm$^2$/s) and $v_{liq}$ is the volume flux of the liquid flow in the nanopore ($v_{liq} \approx 0.05$ cm/s for $q''_m = 100$ W/cm$^2$). Equation (1.8) yields that

$$c_{in} = c_0 \exp \left( \frac{v_{liq} t_m}{D_c} \right)$$

where $c_{in}$ and $c_0$ are the concentrations of contaminants at the interface and in the flushing flow underneath the membrane, respectively, and $t_m$ is the membrane thickness. The Péclet number of the system can be defined as $Pe_c = v_{liq} t_m / D_c$. The contamination level at the interface increases sharply with larger $Pe_c$ and the thinner the membrane, the smaller $Pe_c$ is. For $q''_m = 100$ W/cm$^2$, with $t_m \sim 200$ nm and $c_0 \sim 3 \times 10^{-6}$ (Sigma-Aldrich, Water for HPLC), we have $Pe \sim 0.1$ and $c_{in} \sim 3.3 \times 10^{-6}$ which ensures a clean liquid-vapor interface during evaporation. This may have more implications for membrane-based water purification applications. Overall, this ultrathin nanoporous membrane enables us to characterize the interfacial heat/mass transfer reliably even for >100 W/cm$^2$ interfacial heat fluxes, which has otherwise been impossible in previous works.
1.3 Thesis Overview

The focus of this thesis is to experimentally characterize and fundamentally understand evaporation. We aim to characterize the interfacial heat flux given a certain working condition. Chapter 1 described the background of this thesis, including the motivation and previous studies as well as the overall concept. Chapter 2 elucidated the modeling framework for evaporation in an air ambient as well as a vapor ambient, with the former being diffusion-driven and the latter being pressure-driven. In Chapter 3, we detailed the fabrication process we used to create the desired structure, the setup that we built and the procedures that we followed to characterize evaporation. We also discussed our experimental results and their implications. In Chapter 4, we showcased a potential application of the ultrathin nanoporous design to thermal management of high power electronics. Finally, in Chapter 5, we summarized the fundamental understanding of evaporation that we gained through both experiments and modeling and possible future directions.
2. Modeling Framework

2.1 Diffusion-Driven Evaporation

When evaporation occurs in an air ambient, our traditional understanding is that without forced or natural convection, Fick’s law of diffusion governs transport:

\[ j = -D_v \nabla \rho \]  \hspace{1cm} (2.1)

where \( j \) is the vapor mass flux, \( D_v \) is the binary diffusion coefficient of the air-vapor mixture and \( \rho \) is the vapor density. Based on energy conservation, we obtain:

\[ \dot{q}'' = -D_v \Delta h_v \nabla \rho \]  \hspace{1cm} (2.2)

where \( \Delta h_v \) is the enthalpy difference between the liquid phase and the vapor phase. This is analogous to Fourier’s law of thermal conduction. Since both of them are linear laws, we utilized the concept of shape factor \( S \) for boundary value problems [48]:

\[ \dot{q}'' = -\frac{D_v (\rho_0 - \rho_\infty)}{A/S} \Delta h_v \]  \hspace{1cm} (2.3)

where \( A \) is the total interface area, \( \rho_0 \) and \( \rho_\infty \) are the density of vapor generated by the interface and in the far field, respectively. We designated \( \delta = A/S \) which can be understood as the effective boundary layer thickness and is purely a geometric factor that scales generally with the characteristic length of the evaporator. \( D_v \) has a temperature dependence [49] and is evaluated at a reference temperature [50]:

\[ T_{ref} = \frac{2}{3} T_0 + \frac{1}{3} T_e. \]  \hspace{1cm} (2.4)
In eq. (2.1), we did not consider the gravitational convection characterized by the Grashof number of the system

\[ \text{Gr} = \frac{g \Delta \rho_m \delta^3}{\rho_m \nu^2} \]  

(2.5)

where \( g \) is the gravitational constant, \( \rho_m \) is the reference density of the air-vapor mixture which calculated as [50]:

\[ \rho_m = \frac{2}{3} \rho_{m,0} + \frac{1}{3} \rho_{m,\infty} \]  

(2.6)

where \( \rho_{m,0} \) is the mixture density at the interface, \( \rho_{m,\infty} \) is the mixture density in the far field, \( \Delta \rho_m = \rho_{m,0} - \rho_{m,\infty} \), and \( \nu \) is the kinematic viscosity of the mixture. In this thesis, we designed the experiment such that \( \text{Gr} < 10^{-3} \) and the gravitational effect is negligible. While eq. (2.1) describes evaporation at low heat fluxes very well [44, 45, 49], it does not apply to high flux cases as the bulk gas flow induced by evaporation becomes significant and in turn enhances the interfacial transport. On one hand, the vapor concentration increases as \( T_0 \) increases, such that the dilute-solution assumption of Fick’s law no longer holds. On the other hand, the bulk flow of the vapor-air mixture can no longer be neglected as the evaporative flux increases. The Péclet number of the evaporation system can be defined as

\[ \text{Pe} = \frac{V_m \delta}{D_v} \]  

(2.7)

where \( V_m \) is the bulk velocity of the air-vapor mixture at the interface. Pe gives the ratio between the convective transport rate and the diffusive transport rate.
Theoretically, these inconsistencies can be reconciled by the Maxwell-Stefan equation [49] which accounts for convective transport. For this binary diffusion problem, we can write

\[ j = -\rho_m D_v \nabla \left[ -\ln (1 - \phi) \right] \]  

(2.8)

where \( \phi \) is the vapor mass fraction and we also assumed the air is static and the pressure of air-vapor mixture is constant. Applying the concept of shape factor again, we have the counterpart of eq. (2.3):

\[ q^* = \frac{D_v \rho_m \Delta h_v}{\delta} \ln \left( \frac{1 - \phi_0}{1 - \phi_w} \right) \]  

(2.9)

where \( \phi_0 \) and \( \phi_w \) are the mass fraction of the vapor at the interface and in the far field respectively. Therefore, we can use eq. (2.9) to describe the interfacial heat flux for diffusion-driven evaporation, not limited to small \( \phi \) or low fluxes.
2.2 Pressure-Driven Evaporation

Besides the vapor concentration gradient, the pressure difference between the interface and the far field can also induce evaporation. The interfacial heat flux during evaporation gives rise to a non-equilibrium region within a few vapor mean free paths to the interface, known as the Knudsen layer [51].

Figure 2-1 Schematic of different mechanisms of evaporation (not to scale). (a) Evaporation driven by diffusion where the total pressure \( P_{\text{total}} \) is constant from the interface to the far field. (b) Evaporation driven by the pressure difference between the far field \( P_{\infty} \) and the vapor generated by the interface \( P_0 \).

Evaporation is considered to be kinetically limited if the dominant transport resistance in the system is the one across the Knudsen layer. When evaporation is driven by concentration gradient in an air ambient (Figure 2-1a), the overall heat and mass transfer across the interface is dominated by the Maxwell-Stefan diffusion outside the Knudsen layer [52]. This is certainly non-ideal for understanding the kinetic limit of steady evaporation. Therefore, to minimize the transport
resistance beyond the Knudsen layer, in this study, we can induce pressure-driven evaporation in
a pure vapor ambient (Figure 2-1b), by regulating the temperature of the interface and the pressure
in the far field.

In the context of evaporation from cylindrical nanopores continuously supplied with liquid and
exposed to a pure vapor ambient, liquid wets the pore wall and flows to the liquid-vapor interface
while experiencing viscous resistance. To sustain evaporation, heat is also supplied to the interface
via conduction through the liquid from the pore wall. The liquid flow in nanopores is driven by
the capillary pressure generated by the curved meniscus. Due to viscous losses in the liquid phase
and the wetting nature of the pore wall, the liquid pressure at the interface is lower than the vapor
pressure, and can even be negative (under tension) [4]. When the interfacial pressure difference is
relatively small, the meniscus is pinned at the top of the pore (M₁ in Figure 2-2a). In this “pinning
regime”, the liquid-vapor interface self-regulates its curvature in response to different working
conditions, which includes the pore wall temperature and liquid supply pressure. When the
meniscus is fully extended and the local contact angle reaches the local receding contact angle (M₂
in Figure 2-2a), the interface holds the maximum pressure difference. While the study of a fully
extended meniscus and evaporation has been of primary interest in many studies [31, 53-55], other
configurations for the meniscus are possible which need to be elucidated. As the working
conditions become severe, such as higher pore wall temperatures or heat fluxes, the meniscus will
recede further into the pore (M₃ in Figure 2-2a). In this “receding regime”, the fully-extended
liquid-vapor interface moves within the pore to self-adjust the transport resistance in both the
liquid and the vapor, and maintain the interfacial pressure difference. In more extreme operating
conditions, the interface region will reach the bottom of the pore, resulting in complete dry-out.
Figure 2-2 (a) Schematic of evaporation from a nanopore: the liquid-vapor interface can change its shape (from M₁ to M₂) or position (from M₂ to M₃) in response to different working conditions. (b) Schematic showing vapor transport from the free molecular regime inside the pore, across the Knudsen layer, to the far field equilibrium regime. (c) Resistance network for the molecular transport inside the pore: the overall transport resistance in the pore is the sum of the surface resistance of the liquid-vapor interface and the geometrical resistance from the pore wall.

To predict the behavior of the interface and quantify evaporation within the pore, we have established a modeling framework for liquid and vapor transport across the pore. The interface region is defined as the liquid above the horizontal plane through the center of the meniscus (Figure 2-2b). A uniform temperature, \( T_0 \), and a pressure, \( P_{\text{li}} \), can be prescribed for the interface region due to its small scale, where spatial variations can be neglected.

The liquid flow from the pore inlet to the interface region is governed by the Hagen-Poiseuille equation [56]:

\[
P_m - P_{\text{li}} = \frac{8\mu_L L_f \dot{m}}{\pi r_p^4 \rho_L} \quad (2.10)
\]

where \( P_m \) is the liquid pressure at the pore inlet (the bottom of the pore), \( \mu_L \) is the liquid viscosity, \( L_f \) is the flow length (Figure 2-2b), \( \dot{m} \) is the mass flow rate across the pore, \( r_p \) is the pore radius and
$\rho_l$ is the liquid density. The interfacial pressure balance is then given by the augmented Young-Laplace equation:

$$P_{vi} - P_h = 2\gamma k + \Pi_d$$

(2.11)

where $P_{vi}$ is the vapor pressure on the interface, $\gamma$ is the surface tension, $k$ is the curvature of the meniscus and $\Pi_d$ is the disjoining pressure [57]. $\Pi_d$ can be calculated from the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory [57-59]:

$$\Pi_d = -\frac{A_{sv}}{6\pi(r_p - r)^3} + \Pi_{el}$$

(2.12)

where $A_{sv}$ is the Hamaker constant between the pore wall and the vapor across the liquid medium and can be obtained from the dielectric constants and refractive indices of the interacting substances [55, 57] and $\Pi_{el}$ is the electrostatic component of the disjoining pressure. For non-polar fluids, $\Pi_{el} = 0$ whereas for polar fluids, it can be evaluated as [60]:

$$\Pi_{el} = \frac{\pi}{8} \left( \frac{kT_0}{Ze} \right)^2 \frac{1}{\left( r_p - r \right)^2}$$

(2.13)

Here, $k$ is the Boltzmann constant, $Z$ is the valence of ions and $e$ is the elementary charge. Using the axisymmetric boundary condition at the center of the meniscus, we can integrate eq. (2.10) from $r = 0$ to $r = r_p - \delta$ to obtain the meniscus shape.

The vapor motions in the Knudsen layer can be analyzed in terms of distribution functions using the Boltzmann transport equation (BTE), as the usual thermodynamic quantities are not necessarily well defined under non-equilibrium. There are three key parameters characterizing the BTE in the Knudsen layer[36, 51]: $\rho_K / \rho_0$, $P_K / P_0$, and $S_K$. Here, $\rho_0$ and $P_0$ are the saturation vapor density...
and pressure at the interface temperature $T_0$, $\rho_K$ and $P_K$ are the vapor density and pressure at the boundary between the Knudsen layer and the far field, and $S_K = u_K / (2RT_0)^{1/2}$, where $u_K$ is the bulk vapor velocity coming out of the Knudsen layer and $R$ is the specific gas constant. Since $(2RT_0)^{1/2}$ is proportional to the sonic speed of the system, $S_K$ can be considered as the pseudo-Mach number.

It was shown in previous theoretical studies [61, 62] that any one of the three parameters uniquely determines the other two through the BTE for the Knudsen layer problem in evaporation. In other words, we have

$$\frac{\rho_K}{\rho_0} = f_1 \left( \frac{P_K}{P_0} \right)$$

(2.14)

$$S_K = f_2 \left( \frac{P_K}{P_0} \right)$$

(2.15)

where the explicit forms of $f_1$ and $f_2$ are determined by the collision models and the boundary conditions of the BTE.

The boundary condition at the liquid-vapor interface is characterized by the evaporation coefficient and condensation coefficient ($\sigma_e$ and $\sigma_c$) [61-63]. At equilibrium, $\sigma_e = \sigma_c = \overline{\sigma}$, analogous to the Kirchhoff's law in thermal radiation [64]. Since the evaporation experiments in this thesis was under near equilibrium conditions ($S_K \ll 1$), we also assumed this equality in our analysis.

To determine only those vapor molecules evaporating from the interface and exiting the pore, by accounting for those molecules that recondense, the vapor transport within the pore also needs to be solved. Adopting a radiative thermal transport analogy (Figure 2-2c), we determine the “apparent evaporation and condensation coefficient” $\overline{\sigma}_p$ at the pore outlet by calculating the “surface resistance” as:
Here, $A_c$ is the cross-section area of the pore, $A_m$ is the total surface area of the meniscus and the transmission probability $\eta$ can be calculated as a function of the reduced transport length $L^* = L/r_p$, where $L$ is the distance between the top of the meniscus and the pore outlet, as shown in Figure 2-2b [65]:

$$
\eta = 1 + \frac{L^2}{4} - \frac{L^*}{4} \sqrt{L^2 + 4} = \frac{\left[ (8 - L^2) \sqrt{L^2 + 4} + L^3 - 16 \right]^2}{72L^* \sqrt{L^2 + 4} - 288 \ln \left( \frac{L^* + \sqrt{L^2 + 4}}{2} \right)}
$$

Note that in the pinning case, $L^* = 0$, $\eta = 1$ and eq. (2.16) simply accounts for the self-condensation effect of the curved interface. The vapor distribution function at the interface $\xi_0$ can be written as [61-63]:

$$
\left. \xi_0 \right|_{n_z>0} = \left[ \sigma_p \rho_0 + (1 - \sigma_p) \int_{u_z<0} \xi_0 \, du \right] \exp \left[ -\frac{u^2}{2RT_0} \right] \frac{1}{(2\pi RT_0)^{3/2}}
$$

where $u$ is the molecular velocity and $u_z$ is its z-component (perpendicular to the interface). The effect of non-unity $\sigma_p$ can be generally accounted for following Meland and Ytrehus [37]. The distribution function for the vapor flow coming out of Knudsen layer can be expressed a drifted Maxwell-Boltzmann distribution:

$$
\left. \xi_k \right|_{n_z>0} = \rho_k \exp \left[ -\frac{(u - u_k)^2}{2RT_k} \right] \frac{1}{(2\pi RT_k)^{3/2}}
$$

where $T_k$ is the temperature of the vapor right outside the Knudsen layer.
To gain intuitions about the Knudsen layer, a case study was carried out considering evaporation of octane from silicon nanopores into a vapor ambient maintained at $T_x = 300$ K. While the modelling framework can be applied to a wide range of working fluids, octane was chosen here due to its relatively large mean free path ($\lambda \sim 1.1 \mu m$ [66] at the working condition) as we require $\lambda \gg r_p$ to result in a free molecular flow in the nanopore [67]. The thermophysical properties of octane were obtained as a function of temperature [68-70]. Since we used the moment method described in [71] to solve the BTE in the Knudsen layer, the results are presented in terms of dimensionless quantities defined as: $T^* = (T - T_x) / T_x$, $j^* = j/[(\rho_0(5RT_x)^{1/2}]$, $h^* = j^*/T^*$, $r^* = r/r_p$, and $z^* = z/r_p$.

In Figure 2-3a, the dimensionless heat/mass flux $j^*$ and heat transfer coefficient (HTC) $h^*$ normalized over the cross-section area of the pore are shown as a function of the dimensionless superheat $T^*$. When $T^*$ is relatively low, evaporation occurs in the pinning regime, where both the flux and the HTC increase as the temperature rises due to a higher intensity of molecular emission. As the superheat increases, the meniscus extends further (Figure 2-3b) until it becomes fully extended. Subsequently, the meniscus will start to recede into the pore. In this receding regime, as the superheat is enhanced further, the receding length increases and with the meniscus further inside the pore, there is a lower probability for the vapor molecules to escape from the pore (Figure 2-3c). Consequently, the increase in flux is less steep and the HTC decreases in the receding regime.

When the receding length equals the total pore length, the meniscus reaches the bottom of the pore and the vapor expands into the liquid causing complete dry-out, an undesirable phenomenon for applications relying on maximizing the rate of evaporation. The interfacial transport is more efficient in the pinning regime than the receding regime due to minimal vapor transport resistance. Therefore, to achieve the highest possible fluxes with relative low superheats, it is more favorable
to keep the liquid-vapor interface pinned at the top of the pore. This framework identifies the transition from the pinning to receding mode of evaporation in nanopores.

Figure 2-3 (a) Dimensionless flux $j^*$ (blue solid line) and heat transfer coefficient $h^*$ (green dash line) vs. dimensionless superheat $T^*$ for the reference case (with the evaporation coefficient fixed at 1, the pore radius at 40 nm and the pore length at 10 μm) (b) Shape of liquid-vapor interface for selected superheats in the pinning regime (c) Dimensionless receding length $L^*$ (blue solid line) and transmission probability $\eta$ (green dash line) vs. dimensionless superheat $T^*$ in the receding regime.

We also studied the effect of different geometric parameters on the regime transition and interfacial flux. In Figure 2-4a and b, $r_p$ and $L_p$ were varied from the reference case, and the corresponding $j^*$ vs. $T^*$ are shown for comparison. In Figure 2-4a, as the pore radius decreases, the capillary pressure ($\sim 1/r_p$) supporting the flow in the nanopore increases. However, the viscous loss inside the pore ($\sim 1/r_p^2$ for a fixed flux) increases faster, which gives rise to an earlier regime transition. On the
other hand, in Figure 2-4b, the regime transition, namely recession of the meniscus can also occur at much lower superheats when longer pores are utilized because it increases the viscous losses in the liquid flow.

Figure 2-4 Effect of (a) pore radius, (b) pore length, (c) evaporation coefficient and (d) receding contact angle on the interfacial transport: \(r_p, L_p, \sigma,\) and \(\theta_r\) were independently varied and the corresponding \(j^*\) as a function of \(T^*\) plots are compared to the reference case where the parameters are set as: \(r_p = 40\) nm, \(L_p = 10\) \(\mu\)m, \(\sigma = 1,\) \(\theta_r = 0^\circ\) and \(\phi = 0.2.\)

It should be noted that evaporation of thin liquid films has been analyzed significantly via both experiments and computational modeling in literature. While the theoretical framework developed in this study is more consistent for the chosen geometry and operating conditions, it does not allow a direct comparison with previous studies that consider significantly different operational and geometric parameters. Furthermore, the evaporation coefficient at the interface (\(\overline{\sigma}\) and the
receding contact angle on the pore wall ($\theta_r$) can also affect the overall rate of evaporation from nanopores. An accurate knowledge of these parameters is necessary to predict the overall performance. Consequently, apart from studying sensitivity to the geometric parameters, we also quantify the effect of $\overline{\sigma}$ and $\theta_r$. In Figure 2-4c, for a given superheat, a smaller $\overline{\sigma}$ corresponds to higher vapor transport resistance and lower interfacial flux, resulting in less viscous loss in the liquid phase. Consequently, recession begins at a higher superheat. On the other hand, in Figure 2-4d when the liquid is less wetting ($\theta_r$ is relatively large), the interfacial transport behaves exactly the same as the perfect wetting case except that the meniscus recedes at a lower superheat.

![Graph](image)

Figure 2-5 Effect of porosity $\phi$ on the interfacial transport from one single pore for select superheats with other parameters the same as in the reference case ($r_p = 40$ nm, $L_p = 10$ $\mu$m, $\overline{\sigma} = 1$ and $\theta_r = 0^\circ$)

To study the effect of the spatial distribution of pores, the interfacial flux is plotted as a function of the porosity for select superheats (Figure 2-5). In general, the porosity, which is not determined by a single pore, i.e., a global parameter, does not influence the interfacial transport over one single
pore significantly. However, the net flux shows a different trend with porosity at different temperatures. We attribute this to the interaction of vapor emerging from a single pore with two other sources of vapor flow, namely the molecules directed back at the interface from the vapor ambient (which has a distribution function of \( \xi \mid z \to \infty, u_x < 0 \)), and the vapor emitted from the neighboring pores. When the superheat is relatively low, the vapor flow from the ambient is significant. Hence, a higher porosity ensures that for each unit cell, there are fewer molecules directed back at the liquid-vapor interface, which favors higher evaporation. When the superheat is relatively high, the vapor flow emitted by neighboring pores is more important. Consequently, lower porosities result in better pore-level transport since the interactions with the neighboring pores are lowered. For an intermediate superheat where the two effects are comparable, there is an optimum porosity to ensure maximum flux from a single pore. Note that the planar close-pack limit is \( \phi \approx 0.907 \), so any porosity beyond that cannot be achieved in practice.

More accurately, we can solve the BTE using the Direct Simulation Monte Carlo (DSMC) method [72] with the variable soft sphere collision model [73] and the Borgnakke-Larsen method [74] to account for the polyatomic effects. This approach to analyze evaporation for polyatomic molecules was first reported by Frezzotti [38] and extended to water molecules by Kinefuchi. The common monatomic kinetic approach underestimates the interfacial heat flux as rotational energies is not considered [38, 51]. The modeling results were detailed and plotted alongside the experimental results in Chapter 3.
2.3 Chapter Summary

We modeled the diffusion-driven evaporation in the air ambient with Maxwell-Stefan equation. Applying the analogy between heat and mass transfer, we reduced the problem to determining the shape factor or the effective boundary layer thickness given the boundary conditions. We showed the importance of convective transport caused by evaporation itself and that Fick’s first law of diffusion no longer applies in the high heat flux regimes. We also presented a theoretical framework to elucidate pressure-driven evaporation from nanopores by solving the BTE in the Knudsen layer to incorporate non-equilibrium effects. Non-local effects arising from phase-change in nanoporous geometries was included as well as the self-regulation of the shape and position of the liquid-vapor interface in response to different operating conditions. By applying the Borgnakke-Larsen method in the DSMC simulation, we were able to account for the polyatomic effect during evaporation.
3. **Fabrication and Characterization**

3.1 **Microfabrication**

The ultrathin nanoporous membrane was microfabricated starting from a double side polished silicon wafer with both side coated with silicon nitride (≈300 nm thick) using low pressure chemical vapor deposition (Figure 3-1a). Deposition was carried out at 800 °C.

![Fabrication Process Diagram](image)

Figure 3-1 Schematic representation of the fabrication process: (a) Low pressure chemical vapor deposition of Si₃N₄. (b) Interference lithography that defines the nanopores and reactive ion etch that transfers the pattern partially into the Si₃N₄ layer. (c) KOH back etching with the front side Si is protected by the Si₃N₄ remaining from (b). (d) Contact pad deposition with shadow masking. (e) Nanopore through etching with shadow masking. (f) Heater/RTD deposition with the same mask alignment as (e).

A nanopore array was patterned in the front silicon nitride layer using interference lithography. Due to its high uniformity, low defect density and fast exposure time, interference lithography was chosen to define the pores. A recipe developed in the MIT NanoStructures Laboratory was used with a He-Cd laser with wavelength $\lambda = 325$ nm [75]. Two coherent light waves was set up to generate the interference pattern, which was recorded in a photoresist layer. This was done in two perpendicular directions to result in a nanoporous pattern. The pitch of the nanopores $p$ was determine by...
where θ is the angle between the two coherent laser beams. In this work, we chose θ = 54° to give $p = 200 \text{ nm}$. The pore diameter is adjustable based on the exposure time and etching recipe. Prior to the exposure, a stack of layers was deposited onto the wafer to minimize the back scattering. We first spin-coated an anti-reflection layer (Brewer Science, XHRiC-16) that is ≈400 nm thick after baking. With e-beam deposition, we then covered the front side of the wafer with 20 nm silicon dioxide. After that, an adhesion layer was spin coated onto the silicon dioxide using XHRiC-16 diluted with propylene glycol methyl ether acetate to yield a thickness of 10 - 20 nm. Finally, a negative photoresist (Brewer Science, NR7-250P) was spin coated and baked to a thickness of 200 nm. With this pre-exposure stack (Figure 3-2), the wafer was then mounted onto a stage exposed to two expanding beams of coherent laser light waves. Following the exposure, the wafer was then post baked and developed to reveal the interference pattern (Figure 3-3).

Reactive ion etching (RIE) with tetrafluoromethane gas (Figure 3-1b) was used transfer the nanoporous pattern into the silicon dioxide layer with the photoresist as the mask first. Then using the silicon dioxide as the mask, the pattern was further transferred into the ARC layer with RIE.
and oxygen plasma (diluted with helium). RIE with tetrafluoromethane gas was then used again to etch the pores into the silicon nitride layer.

![SEM image of cross-section of nanopores patterned in photo resist](image)

Figure 3-3 SEM image of cross-section of nanopores patterned in photo resist

The silicon nitride layer was not etched through, which protected the front side when the sample was etched from back side using potassium hydroxide (KOH) solutions (Figure 3-1c). After that, two gold contact pads were deposited onto the sample with e-beam evaporation and shadow masking (Figure 3-1d). Using another shadow mask, we etched through the pores from the front side with RIE and deposited a gold layer to serve as the resistive temperature detector (RTD) as well as the heater (Figure 3-1e, f).

Figure 3-4a shows a sample nano device that we microfabricated with the clean process. The free-standing membrane, connecting two gold contact pads (Figure 3-4a) is of thickness $t_m \approx 200$ nm. The active part of the membrane, located in the middle, is $3.4 \text{ mm} \times 0.28 \text{ mm}$, coated with $40$ nm gold (Figure 3-4b). The nanoporous pattern with pore diameter $d_p \approx 140$ nm and porosity $\approx 0.43$ ($>20,000,000$ pores) was defined in this active area using interference lithography (Figure 3-4c),
while the rest of the membrane was kept non-metallic and impermeable. The large number of pores ensures high signal (evaporation) to noise (heat loss) ratios during the experiment.

Figure 3-4 (a) Image of device with two gold contact pads connected by a free-standing membrane (~200 nm thick). (b) Magnified view of free-standing membrane where the central part is porous and coated with gold. (c) SEM image of the nanoporous membrane with ≈140 nm diameter pores.
3.2 Experimental Procedure

During operation, liquid flowed across the membrane and wicked into the nanopores, where it was resistively heated by the gold layer and evaporated into the ambient. We set the input heating power and waited for the system to equilibrate at a certain temperature. Our system inherently contained a feedback loop. As we set the heating power to a higher value, the membrane temperature also increased, which gave rise to more intense evaporation and a higher cooling rate. When the cooling rate matched the heating power, the system reached a steady state. The response time of the system during the experiment was within one second due to the small thermal mass of the evaporator, and we maintained the steady state for five minutes before recording the data.

3.2.1 RTD Calibration

Prior to the experiment, the resistance of the gold layer was calibrated to an industrial temperature sensor (Omega P-L-A-1/4-6-1/4-T-6) in a gravity convection oven (VWR 1370GM).

Figure 3-5 Sample RTD calibration plot of $T_R$ vs $R_{sample}$: the experimental data (red diamonds) are fitted to a linear model (black dashed line).
We set the oven temperature with its own controller and waited for >2 hours for thermal equilibrium in the oven. The resistance of the gold layer ($R_{\text{sample}}$) and the reference temperature sensor reading ($T_R$) were both obtained by a data requisition device (National Instruments 9226) with a four-wire method. A sample calibration curve was shown in Figure 3-5. We fitted a linear model (black dashed line) to the experimental data. The industrial temperature sensor comes with an error of 0.25 K for this temperature range considered in the present study, and the linear fit caused an additional error of 0.45 K. The overall temperature measurement was then $(0.25^2 + 0.45^2)^{1/2} \approx 0.52$ K in the vapor ambient experiment. For the air ambient experiment, the RTD was calibrated to a T-type thermocouple prior to the experiment and the overall error of the temperature measurement was 1.4 °C.

3.2.2 Heat Loss Characterization

To characterize the heat loss of the system, we fabricated a control sample which has the same structure as the designed device except that the active part is also impermeable. With liquid supplied at 1 mL/min (same as in the evaporation experiment), we measured the heating power $Q_{\text{loss}}$ as a function of the temperature rise of the membrane of the control sample $\Delta T$ as the sample was cooled down by convection and conduction. $Q_{\text{loss}}$ is plotted as a function of $\Delta T$ in Figure 3-6 and the experimental data (red triangles) are fitted to a linear model (black dashed line) $Q_{\text{loss}} = C\Delta T$, which give $C = 4.7 \pm 0.1$ mW/K for the vapor ambient setup and $4.50 \pm 0.03$ mW/K for the air ambient setup.

3.2.3 Setup in Air

We first performed characterization in the air ambient. The microfabricated samples of the same geometry (Sample 1-3) each were placed in a custom-designed test rig which was sealed to the air ambient and had a liquid feed-through and electrical connections.
Figure 3-6 Heat loss characterization using a control sample with impermeable membrane. \( Q_{\text{loss}} \) is plotted as a function of \( \Delta T \) and the experimental data (red triangles) are fitted to a linear model (black dashed line): 
\[
Q_{\text{loss}} = C\Delta T,
\]
which gives \( C = 4.7 \pm 0.1 \text{ mW/K} \).

Figure 3-7 (a) Schematic of the experimental setup: the ultra-thin nanoporous evaporator is placed into a custom-designed test rig sealed to the ambient, facing downwards: DI water flows by the membrane at a constant flow rate (1 mL/min); heat is resistively applied to the gold layer to induce evaporation while the voltage and current is being monitored by a data acquisition system using a four-point measurement. (b) Image of the test rig with a liquid feed-through and electrical connections.
The inlet flow rate was maintained at 1 mL/min using a peristaltic pump, and deionized water was chosen as the working fluid. As our samples sit in the air ambient prior to the experiment for more than a day and water only partially wets gold that is exposed to the laboratory air due to hydrocarbon adsorption [76, 77], the working fluid does not flood the nanoporous membrane surface. A four-point measurement was utilized to monitor the resistance of the RTD and the power input to the heater. We then tested the ultra-thin nanoporous membrane evaporator with the same inlet flow rate (1 mL/min), heating the sample to induce evaporation while monitoring the membrane temperature $T_s$. The air ambient was quiescent at $T_\infty = 22.8 \, ^\circ C$ and the relative humidity was 33%, such that the ambient water vapor density was $\rho_\infty = 0.00672 \, \text{kg/m}^3$.

3.2.4 Setup in Vapor

To perform characterizations in the pure vapor ambient, the device was placed in an environmental chamber to enable controlled temperature and vapor pressure (Figure 3-8a, b). A similar custom test fixture interfaced the device to the liquid ports, electrical connections, and facilitates visualization to ensure that liquid did not flood the membrane surface (Figure 3-8c).

We prepared a liquid reservoir tank which was filled with deionized water (Sigma-Aldrich, Water for HPLC) and then heated to $> 100 \, ^\circ C$ for thermal degassing. The liquid reservoir was subsequently sealed from the ambient. During experiment, the environmental chamber was first pumped down to $<0.5 \, \text{Pa}$ (confirmed by MKS 925 Micro Pirani™ vacuum transducer) and then backfilled with pure water vapor from the reservoir. The vapor pressure in the far field was regulated by the chamber wall temperature and measured by a capacitance pressure transducer (MKS 740C Baratron® Manometer). With a peristaltic pump (Masterflex UX-77921-77), the inlet flow rate was maintained at 1 mL/min. We applied a four-point method to measure the total Joule heating power and read the interface temperature from the RTD. We characterized evaporation
with three ambient vapor pressures: $P_\infty = 2.643$ kPa, $4.935$ kPa, and $10.428$ kPa, and the associated saturation temperatures are $T_\infty = 22.0$ °C, $32.6$ °C, and $46.6$ °C, respectively.

Figure 3-8 Experimental setup. (a) Schematic showing device placed in a custom test fixture in an environmental chamber which allows for liquid feedthrough, electrical connection, and visualization. (b) Image of experimental setup. (c) Image of the nanoporous membrane device during an experiment

3.3 Experimental Challenges

The major experimental challenges had to do with poor mechanical strength of the membrane structure. Given a pressure difference across the membrane, the stress induced in the material scales with $t_m^{-2}$ [78]. The largest stress that the membrane structure can tolerate is determined by the material. Consequently, the ultrathin membrane can only sustain a small amount of pressure difference ($\sim 1$ kPa), which creates a lot of difficulties in both the fabrication process and experimental characterization.
3.3.1 Membrane Fabrication

After the KOH etch, the silicon nitride membrane, which was <300 nm thin, formed a suspended structure as shown in Figure 3-9. However, to pattern the heater/RTD on the suspended structure is challenging. The usual photolithography relies on spin coating photo resist on top of the wafer. The fact that the membrane can only sustain ~1 kPa pressure difference makes it difficult. One potential solution is to tape the working wafer to a carrier wafer and spin the carrier wafer instead. However, releasing the working wafer from the carrier wafer often involves chemicals that generate bubbles and the burst of bubbles can break the membrane. We ended up using shallow masking to pattern the contact pads and the heater/RTD.

Figure 3-9 Wafer coming out of KOH solution with free standing silicon nitride membrane
3.3.2 Boiling Limit

In the chamber experiment, since the flow resistance from the location underneath the membrane to the chamber outlet was very small. The liquid pressure underneath the membrane was close to the saturation pressure at $T_\infty$, which indicates that there existed superheating during evaporation. As we put more and more power into the system, the superheat became higher and higher and eventually nucleation occurred underneath the membrane as shown in the schematic in Figure 3-10. The burst of these bubbles then destroyed the membrane structure, which is the boiling limit of our system. The poor strength of the membrane, on the other hand, prevents us from pressurizing the liquid to suppress the bubble nucleation. To extend the experimental curves in the current study, we will need to interface the thin membrane with supporting structures such as microchannels to decrease the span of the thin membrane and increase the mechanical strength of the thin membrane.

Figure 3-10 Schematic of nucleation underneath the membrane evaporator
3.3 Results and Discussion

The interfacial heat flux \( q'' \) during operation was recorded as

\[
q'' = \frac{Q - C\Delta T}{A}
\]

where \( Q \) is the total Joule heating power, \( A \) is the total interface area (pore area) and \( \Delta T = T_0 - T_\infty \), where \( T_0 \) is the membrane temperature and \( T_\infty \) is the temperature of the ambient.

3.3.1 Air Experiment Results

We first investigated the evaporative transport in the air with relatively low interfacial heat fluxes and plotted \( q'' \) as a function of \( D_v (\rho_0 - \rho_\infty) \Delta h_v \) which is the product of several temperature dependent properties in Figure 3-11.

![Figure 3-11](image)

Figure 3-11 Measurement of the effective boundary layer thickness \( \delta \approx 12.8 \mu\text{m} \) at low evaporative fluxes: the heat flux averaged over the interface area \( q'' \) is plotted against temperature dependent \( D_v (\rho_0 - \rho_\infty) \Delta h_v \). The red triangles, black squares and purple diamonds are the experimental data from Sample 1, Sample 2 and Sample 3 respectively. The gray dash line represents the results from the Fick’s law with \( \delta \) as the fitting parameter.
As predicted by Fick’s law eq. (2.3), there is a linear relationship between the two quantities and we fit the experimental data to a line, where $\delta^{-1}$ can be obtained from the slope. However, the water vapor concentration increases as the interface temperature $T_0$ increases, such that the dilute-solution assumption of Fick’s law no longer holds.

Figure 3-12 (a) Relative deviation from the Fick’s law $\Delta_{\text{Fick}}$ vs the mass fraction of the water vapor at the interface $\phi_0$. (b) Relative deviation from the Fick’s law $\Delta_{\text{Fick}}$ vs the Péclet number of the system $Pe$.

Figure 3-12a plots the relative deviation of the experimental data from the Fick’s law prediction $\Delta_{\text{Fick}}$ as a function of the mass fraction of the vapor at the interface $\phi_0$, where $\Delta_{\text{Fick}}$ is generally less significant when $\phi_0$ is smaller. On the other hand, the bulk flow of the vapor-air mixture can no longer be neglected as the evaporative flux increases. Figure 3-12b plots $\Delta_{\text{Fick}}$ against the Péclet number of the system. Since eq. (2.3) does not account for convection, $\Delta_{\text{Fick}}$ turns larger as $Pe$ increases.
Therefore instead of using Fick’s law, we model the interfacial transport in the high flux regime with the Maxwell-Stefan equation [49] for this air-vapor diffusion problem (eq. (2.9)).

![Graph showing interfacial heat flux as a function of membrane temperature.](image)

Figure 3-13 The interfacial heat flux $q''$ as a function of membrane temperature $T_0$ over a large range of evaporative heat fluxes: the red triangles, black squares and purple diamonds are the experimental data from Sample 1, Sample 2 and Sample 3, respectively. The blue dash line and the pink solid line represent the model prediction from Fick’s law and the Maxwell-Stefan equation, respectively, where both models use the same $\delta$ measured from Figure 3-11.

Figure 3-13 shows the interfacial heat flux $q''$ as a function of membrane temperature $T_0$ over a large range of evaporative heat fluxes. The predictions from eq. (2.3) generally underestimates the interfacial heat flux in the experiments and the linear behavior observed in Figure 3-11 was not maintained in the high flux regime. To plot eq. (2.9) (pink solid curve in Figure 3-13), we used the same $\delta$ measured from Figure 3-11 as it is only a geometric factor, which agrees well with the experimental data over the whole range of interfacial fluxes. Indeed, Equation (2.3) is just the limiting case of eq. (2.9) and the enhanced convective transport further facilitates the interfacial heat/mass transfer in the high flux regime. With our evaporation into air experiment, we
experimentally demonstrated the validity of the Maxwell-Stefan equation and that it is possible to reach high interfacial heat fluxes (~500 W/cm²) with pure evaporation. We note that the high flux evaporative transport was assisted by the small boundary layer thickness $\delta$. If we scale up the system, this $\delta$ will become larger, which can increase the vapor diffusion resistance.

3.3.2 Vapor Experiment Results

To eliminate vapor diffusion resistance and realize kinetically limited evaporation, we characterized evaporation in a vapor ambient with vapor pressures: $P_\infty = 2.643$ kPa, 4.935 kPa, and 10.428 kPa, and the associated saturation temperatures are $T_\infty = 22.0$ °C, 32.6 °C, and 46.6 °C, respectively. The interfacial heat flux $q''$ is shown in as a function of the temperature rise $\Delta T$ for these working conditions in Figure 3-14.

![Figure 3-14 Experimental results of interfacial heat flux $q''$ as a function of temperature rise $\Delta T$ for select ambient temperatures. The green crosses represent the results from evaporation into an air ambient reported in our previous work[52], and the red triangles, blue squares, and brown dots are the evaporation data in](image)
the present study of evaporation into a vapor ambient for $T_\infty = 22.0 \, ^\circ C$, 32.6 $^\circ C$, and 46.6 $^\circ C$, respectively. The error bars in $\dot{q}''$ are smaller than the symbol size.

The green crosses represent the results from evaporation into an air ambient reported in the previous section. The red triangles, blue squares, and brown dots are the evaporation data in the present study of evaporation into a vapor ambient for $T_\infty = 22.0 \, ^\circ C$, 32.6 $^\circ C$, and 46.6 $^\circ C$, respectively. Comparing the red triangles to the green crosses, we note that for similar far field vapor temperatures, the heat transfer coefficient ($h = \dot{q}'' / \Delta T$) associated with evaporation into vapor is much higher than that in the air, because the former is kinetically limited and the latter is diffusion limited. Furthermore, among different working conditions for evaporation into vapor, $h$ increases significantly as $T_\infty$ increases. For $T_\infty = 46.6 \, ^\circ C$, $h$ can be as high as 54 W/cm$^2$ K.

We define a dimensionless interfacial flux:

$$\bar{q}'' = \frac{P_K}{\rho_0} S_K.$$  \hspace{1cm} (3.3)

From eqs. (2.14) and (2.15), $\bar{q}''$ is uniquely determined by $P_K/\rho_0$. The gas dynamics outside the Knudsen layer requires that when $S_K \ll 1$, $P_K = P_\infty$ for the vapor flow expanding from the membrane into the chamber [79]. Therefore, equivalently, $\bar{q}''$ is just a function of $\Delta P/\rho_0$, where $\Delta P = P_0 - P_\infty$. This signifies that the evaporative flow is driven by the pressure difference and predicts that with proper normalization, the experimental data (in vapor) should all collapse onto one curve when plotted against $\Delta P/\rho_0$. From energy conservation,

$$\bar{q}^* = \frac{\dot{q}^*}{\rho_0 \sqrt{2RT_0 \Delta h_v}}$$  \hspace{1cm} (3.4)

54
Note that denominator in eq. (3.4) is proportional to the sonic limit of the interfacial heat flux. After this nondimensionalization, in Figure 3-15, the evaporation data for different working conditions all fell upon a single curve (red triangles, blue squares, and brown dots).

![Figure 3-15](image)

Figure 3-15 Dimensionless interfacial flux $\tilde{q}''$ as a function the dimensionless deviational pressure $\Delta P / P_0$. The red triangles, blue squares, and brown dots represent the experimental data in the present study for $T_\infty = 22.0 \, ^\circ C$, $32.6 \, ^\circ C$, and $46.6 \, ^\circ C$, respectively. The solid black line is the DSMC modeling result with $\sigma_e = \sigma_c = 1$ and the black dashed line is the best fit with equal evaporation and condensation coefficients, which gives $\sigma_e = \sigma_c = 0.32$. The error bars in $\tilde{q}''$ are smaller than the symbol size.

This collapse shows that the interfacial transport, in the dimensionless sense, is purely determined by this single system parameter $\Delta P / P_0$. This agrees with the prediction from our analysis of the Knudsen layer and indicates that evaporation was indeed kinetically limited. It also explains why $h$ is higher for higher $T_\infty$ in Figure 3-14, as $\rho_0$ increases sharply with temperature. Accordingly, $\rho_0 (2RT_\infty)^{1/2} \Delta h_{iv}$ can be thought as the figure of merits of evaporative heat transfer when choosing working fluids given a working condition. We also plotted the DSMC simulation results for $\tilde{q}''$ as a function of $\Delta P / P_0$ with $\sigma_e = \sigma_c = 1$ (black solid line in Figure 3-15), which drastically overestimates the interfacial heat flux and indicates that there are non-idealities at the interface. The dashed line
in Figure 3-15 represents the least-square model fit with equal evaporation and condensation coefficients, which gives $\sigma_e = \sigma_c = 0.32 \pm 0.04$. Molecular dynamics simulations of water generally yielded $\sigma_e$ and $\sigma_c$ on the same order of magnitudes, although various values have been reported [40-42]. On the other hand, although the current work obtained similar $\sigma_e$ and $\sigma_c$ for water compared to several previous experimental studies [80, 81], it actually represented quite different interfacial heat and mass transfer as the non-equilibrium and polyatomic effects were generally not taken into account when interpreting the experimental data in prior works.
3.4 Chapter Summary

We microfabricated the ultrathin nanoporous membrane with the help of interference lithography and standard clean room processes. We experimentally characterized evaporation from the membrane in both an air ambient and a vapor ambient. The interface temperature was closely monitored by the RTD on top of the membrane. Heat loss was properly taken into account in the analysis. With the experiment in the air, we showed that it is possible to reach high interfacial heat fluxes (~500 W/cm²) with pure evaporation and experimentally demonstrated the validity of the Maxwell-Stefan equation even when the interfacial heat flux is high. In the vapor experiment, we enabled kinetically limited evaporation. With both experiments and modeling, we demonstrated that the kinetic limit of evaporation is a function of the pressure ratio between the far field vapor and that generated by liquid-vapor interface. We achieved high interfacial heat transfer coefficients (54 W/cm² K for \( T_v = 46.6 \, ^\circ C \)) and more generally, showed that \( h \) scales with \( \rho_0 (2RT_0)^{1/2} \Delta h_v \) and becomes higher for higher vapor ambient temperatures. We determined the evaporation and condensation coefficients from the experimental data with a kinetic model that accounted for the non-equilibrium and polyatomic effects.
4. Application in Thermal Management

4.1 Thermal Management Challenges

Thermal management has become a critical issue in the semiconductor industry due to the increasing power density of microprocessors, laser diodes and power amplifiers [82-84]. One of the most pressing challenges in current and next-generation electronics is heat removal of wide band gap semiconductors based on gallium nitride (GaN) and silicon carbide (SiC), for high-power radiofrequency (RF) applications [85]. For example, monolithic microwave integrated circuits (MMICs) based on GaN high electron mobility transistor (HEMT) technology are devices of particular importance for microwave applications. With a standard layout [86] (Figure 4-1a, b), and a modest power density of 5 W/mm, the heat flux generated over the gate area in the RF MMIC highlighted by the red stripes in (0.5 μm × 150 μm each), can be as high as 1000 kW/cm² [87]. Even on the backside of the die, the heat flux can still be > 1 kW/cm² [87]. Such high fluxes are likely to induce high temperatures in the gate area, which can reduce the lifetime and the reliability of the GaN HEMT devices [85].

A common technique to cool GaN HEMTs is to use a single-phase microchannel cooler. For example, Calame et al. demonstrated that die-level heat transfer coefficients (HTCs) of 0.021 kW/cm²-K can be achieved with 1.9 L/min water flowing through copper microchannels [85]. With such microchannel coolers rejecting heat to a reservoir maintained at 25 °C, we simulated the heat conduction in the device to determine temperature and the heat flux distribution in the GaN HEMT (Figure 4-1a, b) using the finite element method in COMSOL Multiphysics [88], where the total number of elements was 4383224 and the relative tolerance for convergence was set as 10⁻⁶. The thermal conductivities of GaN and SiC (kGaN and kSiC) and the thermal boundary resistance (Rθ) between these layers, as a function of temperature, were taken into account as [89]:

58
\[ k_{\text{GaN}} = 150 \left( \frac{T}{300 \text{ K}} \right)^{-1.4} \text{ (W/m-K)} \]  

(4.1)

\[ k_{\text{SiC}} = 420 \left( \frac{T}{300 \text{ K}} \right)^{-1.4} \text{ (W/m-K)} \]  

(4.2)

\[ R_b = 1.57 \times 10^{-15} \left( \frac{T}{1 \text{ K}} \right)^{2.76} \text{ (m}^2\text{K/W)} \]  

(4.3)

Using the typical heat fluxes encountered in GaN HEMT (1000 kW/cm\(^2\) over the gate area) and the HTC achievable using single-phase microchannel cooling, the temperature profile for a quarter of the die is shown in

On the other hand, phase change cooling can be more effective, taking advantage of the enthalpy of vaporization and lowering the pumping power requirement. However, phase-change cooling mechanisms, such as pool-boiling, are fundamentally limited by the critical heat flux (CHF), which has been demonstrated to be \( \sim 300 \text{ W/cm}^2 \) in literature [90]. On the other hand, while flow boiling is promising for reducing the pumping power, and achieving a higher HTC and heat flux, flow instabilities [91], temperature and pressure fluctuations [92] are still unresolved concerns.

Another approach that makes use of the heat of vaporization is the implementation of thin film evaporation [4, 93]. In this case, the thermal resistance across the evaporating liquid is minimized by maintaining a thin liquid film across which the overall thermal transport is significantly enhanced. However, active pumping of liquid into the evaporating thin film (< 1 \( \mu \text{m} \) thick [54]) over large regions can be impractical due to high pressure drops, requiring significant pumping powers. Consequently, to facilitate passive liquid flow, nano/micro wicks have been utilized to generate capillary pressure to draw liquid into the evaporating thin film region [94]. However, as the characteristic wicking size is made smaller, the capillary pressure and the viscous loss both
increase. As a result, in typical microfluidic implementations of thin film evaporation, these two parameters are strongly coupled, limiting the overall performance.
4.2 Device Design

The ultrathin nanoporous configuration (supported by microchannels with characteristic dimension < 10 μm) can decouple the viscous stress and the capillary pressure.

Figure 4-1 (a) Standard lay-out of the reference GaN HEMT described in Ref. [86] (b) Schematic of the cross-section and boundary conditions for GaN HEMT with a silicon microchannel cooler. The temperature dependence is taken into account for thermal conductivities of GaN and SiC and the thermal boundary resistance between them [89]. The inward heat flux and the heat transfer coefficient for silicon microchannel cooler are adapted from Ref. [85] (c) Temperature profile in the GaN HEMT including both the GaN die and the SiC substrate and (d) heat flux distribution at the backside of the SiC substrate when it is attached to a copper microchannel cooler with a heat transfer coefficient of 0.021 kW/cm²-K [85] rejecting heat to a 25 °C reservoir (e) Cross-section and (f) bottom view schematic of proposed cooling device attached to the GaN HEMT die: liquid is routed into microchannels and wicks into nanopores of a membrane supported by channel walls; heat is conducted across the substrate, via the channel walls, within the membrane and to the liquid-vapor interface where evaporation occurs. The evaporated working fluid condenses at a condenser and is then circulated back to the inlet of the cooling device.

The heat supplied for evaporation conducts across the substrate to the microchannel walls, then through the membrane to the liquid-vapor interface, where evaporation takes place (Figure 4-1e). The device relies on the capillary pressure supplied by the nanopores to drive the flow, and takes advantage of phase change to dissipate significant amounts of heat. This is done while minimizing
the viscous losses for the flow across the microchannels and the membrane, and the overall thermal resistance across the liquid. Consequently, the device can potentially deliver high heat fluxes for cooling, with low overall temperature differences as well as minimal pumping power requirements. The reliance on the capillary pressure within the pores to drive the flow also results in a self-regulating device, which may be able to better address challenges associated with spatially-varying heat fluxes in flow-boiling based approaches, such as pressure instabilities and flow mal-distribution, which may be particularly challenging to mitigate at the microscale.
4.2 Coolant Selection

In Chapter 2, we found that the interfacial heat transfer is most efficient when the meniscus is pinned at the top of the pore with total accommodation ($\sigma = 1$ which is more likely for non-polar working fluids [95-98]) and the figure of merits for evaporative transfer is $\rho_0 (2RT_0)^{1/2}\Delta h_{lv}$. We normalized this quantity to the value of water at 25 °C and denoted this as

$$\Pi_1 = \frac{\rho_0 \sqrt{2RT_0 \Delta h_{lv}}}{(\rho_0 \sqrt{2RT_0 \Delta h_{lv}})_{\text{water}}}$$  \hspace{1cm} (4.4)

A larger $\Pi_1$ indicates better interfacial heat transfer, which favors working fluids not only with a high $\Delta h_{lv}$, but a high $\rho_0$ as well. On the other hand, since we rely on the capillary pressure to overcome the viscous loss, we define the liquid transport factor $\Pi_2$ as done in heat pipes [99]:

$$\Pi_2 = \frac{\gamma_p \Delta h_{lv}}{\mu_t} \left/ \left( \frac{\gamma_p \Delta h_{lv}}{\mu_t} \right)_{\text{water}} \right.$$  \hspace{1cm} (4.5)

This is also normalized to the properties of water at 25 °C. For the same rate of heat removal, a larger $\Pi_2$ indicates that the device is less prone to dry out. Figure 4-2a shows these two figures of merit ($\Pi_1$ and $\Pi_2$) for select working fluids. Compared to other working fluids, R134a has a much higher $\Pi_1$. While $\Pi_2$ for R134a, R245fa, pentane, and methanol is comparable, it is significantly higher for water. We chose R134a to carry out device performance analysis, despite its higher risk of dry-out, due to its exceptionally high cooling potential Figure 4-2b. However, it should be noted that the same computational methodology is indeed applicable for any other working fluid, and can be utilized to determine device performance following a similar procedure.
Figure 4-2 (a) Figures of merit for different working fluids: liquid transport factor $\Pi_2$ vs. interfacial transport factor $\Pi_1$ (both normalized to the properties of water). (b) Interfacial heat transfer coefficient from nanoporous membrane normalized over pore cross-section area as a function of temperature difference between evaporating surface and far field vapor ($T_e = 25$ °C) with $\bar{\sigma} = 1$ for different working fluids.
1.3 Device Model

We modeled the pressure drop and heat transfer for the entire cooling device, after choosing R134a as the coolant and determining the pore-averaged evaporative boundary condition (Figure 4-2b). The pressure drop in the microchannels and nanopores are determined as:

\[
\frac{dP_i}{dx} = \frac{f \text{Re}}{4D_h^2} \mu V_i
\]  

where \( P_i \) is the pressure in the liquid phase, \( x \) is the flow length, \( D_h \) is the hydraulic diameter [56], \( f \text{Re} \) is the Poiseuille number which depends on the channel cross-section shape [100] and \( V_i \) is the bulk liquid velocity. Assuming that R134a perfectly wets the pore due to its low surface tension, the capillary pressure is:

\[
P_c = \frac{4\sigma}{d_p}
\]  

where \( d_p \) is the pore diameter. We define a dimensionless pressure budget \( P_B^* \) as the difference between the capillary pressure and the total pressure drop normalized over the capillary pressure:

\[
P_B^* = \frac{P_c - \int \frac{dP_i}{dx} \, dx}{P_c}
\]  

For operating conditions with \( P_B^* < 0 \), the cooling device will dry out due to insufficient liquid supply to the evaporating region.

The heat transfer in the proposed device can be analyzed as a two-dimensional problem, due to the periodic geometry of the cooling device (Figure 4-1e). Figure 4-3a depicts the boundary conditions
for a unit cell, marked by the dotted box in Figure 4-1e. The governing equation for the steady-state heat conduction across the cooling device is:

$$\nabla \cdot (k_i \nabla T) = 0$$  \hspace{1cm} (4.9)

where $T$ is the temperature across the unit cells, $i = 1, 2, 3, 4$. $k_1$, $k_2$, $k_3$ and $k_4$ denote the thermal conductivity of the substrate, the channel wall, the porous membrane and the working fluid, respectively. The cooling device was designed in silicon to take advantage of the wide range of microfabrication techniques available for silicon substrates. However, the modeling done in this work can be readily translated to other substrate materials. The temperature dependence of thermal conductivities of silicon and R134a is taken into account as described in Ref. [89] and [101]. The thermal conductivity of the microchannel walls and the nanoporous membrane ($k_2$ and $k_3$) also depends on the limiting dimension of these structures [102]. Therefore, in this study, the size dependence of $k_2$ and $k_3$ was interpolated from the analyses carried out in Ref. [102].

In Figure 4-3a, a uniform heat flux $q'_{d}$ is applied at the bottom of the unit cell, while a pore-averaged evaporative heat transfer coefficient $h_{in}$ is applied on top of the membrane, considering the membrane porosity $\phi$. All other boundaries are assumed to be adiabatic and $T_\infty$ is set at 25 °C. Note that a portion of the silicon substrate (1 μm) is also included in the heat transfer model to account for the constriction resistance from the silicon substrate to the channel walls. Equation (4.9) was solved iteratively using finite element method in COMSOL Multiphysics due to the nonlinearity arising from the temperature dependence of $k_i$ ($i = 1, 2, 3, 4$) and $h_{in}$. The total number of elements in COMSOL was 13259 in this case and the relative tolerance was set to be $10^{-6}$.

To calculate the pressure budget, we first set $q'_{d} = 1$ kW/cm$^2$, porosity = 0.25, $d_p = 100$ nm, the membrane thickness $t_m = 300$ nm, the microchannel width $w = 5$ μm, the channel aspect ratio
(width: depth) $AR = 1$, the channel wall solid fraction $SF = \frac{t_w}{w + t_w} = 0.2$, where $t_w$ is the channel wall thickness. $P_B^*$ was then found to be 0.3423, which indicates that dry-out will not occur for these operating conditions. The temperature profile in the cooling device is plotted in Figure 4-3b, which allows evaluation of the overall HTC of the cooling device:

$$h_d = \frac{q''}{T_b - T_w}$$  \hspace{1cm} (4.10)

where $T_b$ is the average temperature at the base of the unit cell (Figure 3 (a)). In this reference case, $h_d = 0.0441 \text{ kW/cm}^2\text{-K}$.

Figure 4-3 (a) Boundary conditions for a device unit cell (the yellow dash box in Figure 4-1e): a uniform heat flux $q''_d$ is applied to the bottom of the unit cell while an evaporative heat transfer coefficient is assigned on top of the membrane where liquid can wick in. All other boundaries are assumed to be adiabatic. Both the working fluid and the solid material were assigned temperature-dependent thermal conductivities and the thermal transport in the channel wall and the membrane was considered as size-dependent. (b) Temperature profile in the unit cell for a reference design with porosity = 0.2, $d_p = 100 \text{ nm}$, $t_m = 300 \text{ nm}$, $w = 5 \text{ \mu m}$, $AR = 1$ and $SF = 0.2$
Apart from the reference case study, a parametric sweep of various device geometries was also conducted, where each geometric parameter, namely porosity, $d_p$, $t_m$, $w$, $AR$ and $SF$ were varied independently from the reference case described above, and the corresponding effects on the heat transfer and pressure drop are shown in Figure 4-4 a-f.

![Figure 4-4](image)

Figure 4-4 Parametric study of $h_d$ (blue dash line) and $P_{th}$ (orange solid line) as functions of (a) porosity, (b) pore diameter $d_p$, (c) membrane thickness $t$, (d) microchannel width $w$, (e) channel aspect ratio $AR$ and (f) channel wall solid fraction $SF$.

In Figure 4-4a, as the membrane becomes more porous by maintaining a constant pore diameter and increasing the number of pores per unit area, $h_d$ first increases due to a larger available evaporation area. Then, it decreases due to a decrease in the effective thermal conductivity of the
membrane. Furthermore, $P_B^*$ increases with porosity, since the mass flux in a single pore decreases with an increase in porosity.

In Figure 4-4b, for all the pore diameters considered, the thermal resistance across the liquid confined within the pore is negligible. However, for a fixed porosity, a larger $d_p$ results in a larger pore spacing, which leads to a higher effective membrane thermal conductivity due to more diffusive thermal transport within the membrane [102]. This results in enhancing the overall heat transfer. On the other hand, since the viscous loss inside the pore scales with $1/d_p^2$ and the capillary pressure scales with $1/d_p$, $P_B^*$ initially increases as $d_p$ increases since the decrease in the viscous loss has a greater effect than the loss in capillary pressure. However, for larger $d_p$, the viscous loss in the pore is much lower than the loss in the microchannel, and therefore does not affect the total pressure drop significantly. Consequently, a continued decrease in the capillary pressure due to a larger $d_p$ causes a decrease in $P_B^*$.

Figure 4-4c shows that as the membrane becomes thicker, the spreading resistance within the membrane becomes smaller, which facilitates improvement in the overall heat transfer. However, this effect plateaus as the spreading resistance contributes less to the total thermal resistance while $t_m$ increases. $P_B^*$ decreases rapidly for thicker membranes due to larger viscous losses for flow through the nanopores.

In Figure 4-4d, with increasing channel width, $w$, the spreading resistance in the membrane increases, which results in performance degradation. Meanwhile, the pressure drop in the microchannels becomes smaller, which enhances $P_B^*$. However, $P_B^*$ becomes insensitive to variation in $w$ once the pressure-drop is mostly due to the flow across the membrane.
A larger AR corresponds to a larger channel height, which results in larger thermal resistance and consequently reduces $h_d$, shown in Figure 4-4e. With a decrease in the flux in the microchannels due to larger flow cross-section area of the channel, $P_B$ increases rapidly until the viscous loss across the membrane dominates.

In Figure 4-4f, as $SF$ increases, the membrane area available to wick liquid decreases. Therefore, the flux in a single pore becomes larger, resulting in a larger pressure drop across the membrane, decreasing $P_B^*$. An increasing $SF$ also decreases the thermal resistance through the channel wall and within the membrane, so $h_d$ is initially enhanced. However, because the net evaporation area becomes smaller, $h_d$ decreases when SF is relatively large.
4.4 Optimization

After understanding the effect of each geometric parameter, a global optimization was performed in the design space (containing all of the geometric parameters), evaluating the heat transfer and pressure drop of each design with $q''_d = 1 \text{ kW/cm}^2$ (Figure 4-5).

Figure 4-5 Global optimization of device geometric design at $q''_d = 1 \text{ kW/cm}^2$: to maximize $h_d$ while maintaining $P^*_B > 0.6$, the geometric parameters are designed as: porosity = 0.4, $d_p = 120 \text{ nm}$, $t_m = 450 \text{ nm}$, $w = 4 \mu\text{m}$, $AR = 2.5$ and $SF = 0.25$. For this optimum design, $h_d$ varies as a function of $q''_d$ (inset).

The criteria for the optimization is determined based on the application of this technology. For this current study, among parametric combinations satisfying $P^*_B > 0.6$, we selected a design which provides the optimum heat transfer performance. With $P^*_B > 0.6$, we aim to mitigate the risk of dry-out caused by fabrication uncertainties, such as merging of nanopores and variation of channel sizes, and non-uniform heat fluxes at the backside of the die (up to $\sim 2 \text{ kW/cm}^2$). The optimum design parameters are given as porosity = 0.4, $d_p = 120 \text{ nm}$, $t_m = 450 \text{ nm}$, $w = 4 \mu\text{m}$, $AR = 2.5$, $SF$
which results in \( h_d = 0.0541 \text{ kW/cm}^2\text{-K} \). Note that this \( h_d \) was obtained only for a constant and uniform heat flux \( (q''_d = 1 \text{ kW/cm}^2) \) dissipated by the evaporative cooling mechanism. Due to the temperature dependence of material properties \( (k_i, i = 1, 2, 3, 4) \) and interfacial transport, \( h_d \) also varies as a function of \( q''_d \) for the chosen geometric design (inset of Figure 4-5). Consequently, \( h_d \) can serve as a non-linear boundary condition when modeling evaporative cooling for the entire GaN HEMT die.

![Figure 4-6](image-url)

**Figure 4-6** (a) Temperature profile in the GaN HEMT die and (b) heat flux distribution at the backside of the cooler with implementation of the proposed cooling device

To demonstrate the feasibility of this proposed device, we model the overall heat transfer by interfacing the GaN HEMT with the optimized evaporative cooling device *via* gold eutectic bonding. To account for the additional thermal resistance due to the gold eutectic bond, we included a 10 \( \mu \text{m} \) gold and 100 \( \mu \text{m} \) silicon layer between the cooling device and the backside of the silicon carbide substrate of the GaN HEMT device. For this configuration, the net heat transfer was again evaluated using the finite element method in COMSOL Multiphysics, where the total number of elements was 4598448 and the relative tolerance for convergence was set as \( 10^{-6} \). The resulting steady state temperature profile across the GaN HEMT device is shown in Figure 4-6a.
When compared with Figure 4-1c, the benefit of implementation of an evaporative cooling device is clear. While the heat flux distribution at the backside of the die (Figure 4-6) is similar to the case with microchannel cooler, the near-junction temperature is reduced by 46 K for the chosen GaN HEMT device by implementing the evaporative cooling device.
4.5 Chapter Summary

We proposed a membrane-based evaporative cooling device for thermal management of high flux electronics. In order to determine an application-specific design and quantify the overall performance, we carried out a detailed thermofluidic analysis. Through the analysis, we identified two non-dimensional quantities, namely the interfacial heat transfer factor and the liquid transport factor, as important criteria for coolant selection. We modeled the overall thermal resistance across the liquid-vapor interface, membrane and the supporting microchannel structure, and the pressure drop associated with coolant supply through the micro/nanofluidic network. A parametric sweep of critical geometries demonstrated the effect of each parameter on the device performance and a global optimization of device design resulted in a HTC of 0.0541 kW/cm²-K to dissipate a heat flux of 1 kW/cm². There is a qualitative trade-off between thermal performance and risk of dry-out. However, by applying detailed computational analysis and optimization for a particular fluid, one can design a device that meets both performance and reliability metrics successfully over a wide range of operating conditions. The proposed design is expected to have an impact on thermal management of high flux power electronics, such as GaN HEMTs, by significantly reducing the near junction temperature (by > 40 K) compared to traditional single-phase microchannel cooling, due to a two-fold increase in the die-level heat transfer coefficient.
5. **Summaries and Future Directions**

We investigated the interfacial transport during evaporation in this thesis. During the completion of this thesis, we identified and addressed several key experimental challenges which include: (1) measuring the interface temperature accurately and non-invasively; (2) decoupling the interfacial thermal resistance from the thermofluidic resistance in the liquid phase and the diffusion resistance in the vapor phase; and (3) mitigating the risk of blockage of evaporating surface due non-evaporative contaminants.

We designed, microfabricated, and characterized an ultrathin nanoporous membrane which allowed us to locally heat the liquid-vapor interface, largely reduce the liquid pressure drop, and closely monitor the temperature of the evaporating surface. We modeled the diffusion-driven evaporation in the air ambient with Maxwell-Stefan equation, accommodating the effects of high vapor concentrations and significant bulk gas velocity. With the experiment in the air, we demonstrated interfacial heat fluxes of \( \approx 500 \text{ W/cm}^2 \) for evaporation in air, where we elucidated that the Maxwell-Stefan equation governed the overall transport instead of Fick’s law, especially in the high flux regime. We analyzed the vapor dynamics in the Knudsen layer under the framework of BTE, accounting for the non-equilibrium and polyatomic effects. We also performed evaporation in a vapor ambient, where we demonstrated that the kinetic limit of evaporation is solely a function of the pressure ratio between the far field vapor and that generated by liquid-vapor interface. We achieved high interfacial heat transfer coefficients (54 W/cm\(^2\) K for \( T_\infty = 46.6 \degree\text{C} \)) and more generally, showed that \( h \) scales with \( \rho_0 (2RT_0)^{1/2} \Delta h_{lv} \) and becomes higher for higher vapor ambient temperatures. The evaporation and condensation coefficients were also determined from the experimental data with a consistent kinetic model.
To construct a general regime map for evaporation, we need three quantities: $P_0$ the saturation pressure at the liquid temperature, $P_v$ the saturation pressure at the ambient temperature, and $P_\infty$ the total ambient pressure. To induce evaporation, either diffusion limited or kinetically limited, we need $P_0 > P_v$. As we are increasing $P_0$ while maintaining $P_v < P_0 < P_\infty$, we have diffusion limited evaporation as in the case in an air ambient (Figure 5-1a). Note that this is not possible for evaporation in pure vapor because $P_v = P_\infty$ in that scenario. Once $P_0$ surpasses $P_\infty$, the vapor generated by the interface can push the ambient gas away, which gives rise to kinetically limited evaporation governed by the BTE in the Knudsen layer. This is as if evaporation occurred in pure vapor (Figure 5-1b). Our study was limited to low Mach number cases due to the boiling limit of the liquid adjacent to the membrane. However, if the configuration is further optimized to allow higher Mach numbers, the gas expansion resistance will play a significant role in the evaporative transport, which will eventually reach the sonic limit. We summarized these different regimes in the schematic in Figure 5-1c. Note that we assumed that the condenser is far away enough from the evaporating surface (outside the Knudsen layer). The current work improves the fundamental understanding of both diffusion limited and kinetically limited evaporation. With this knowledge at the interface level, we showed the significant promise of applying the ultra-thin nanoporous configuration to thermal management of high flux electronics with a membrane-based evaporative cooling device design.
Figure 5-1 Schematic of different regimes of evaporation (not to scale). (a) Evaporation in air where the far field vapor concentration is lower than that at the interface and the transport resistance associated with gas diffusion ($R_{\text{diffusion}}$) is much greater than that across the Knudsen layer ($R_{\text{kinetic}}$). (b) Evaporation in vapor where the far field pressure is lower than that at the interface and the transport resistance associated with gas expansion ($R_{\text{diffusion}}$) is much greater than $R_{\text{kinetic}}$, which allows us to focus on $R_{\text{kinetic}}$ in this study (red box). (c) Schematic of regime map of evaporative heat flux as a function of $P_0/P_\infty$, where $P_0$ is the saturation vapor pressure at the interface and $P_\infty$ is the total pressure in the ambient. To induce evaporation, either diffusion limited or kinetically limited, we need $P_0 > P_\nu$, where $P_\nu$ is the saturation vapor pressure in the ambient. As we are increasing $P_0$ while maintaining $P_\nu < P_0 < P_\infty$, we have diffusion limited evaporation as
in the case in an air ambient. Note that this is not possible for evaporation in pure vapor because $P_v = P_\infty$ in that scenario. Once $P_\infty$ surpasses $P_\infty$, the vapor generated by the interface can push the ambient gas away, which gives rise to kinetically limited evaporation governed by the BTE in the Knudsen layer. Our study was limited to low Mach number cases due to the boiling limit of the liquid behind the membrane. However, if the configuration is further optimized to allow higher Mach numbers, the gas expansion resistance will play a significant role in the evaporative transport, which will eventually reach sonic limit.

Figure 5-2  Cross-sectional schematic of supported membrane structure from [5]. Liquid flows through a series of manifold channels (shown in green) and is wicked into the liquid supply channels (shown in red)
before flowing through the membrane pores and evaporating from the membrane surface. Key dimensions are also provided in the schematic.

Future directions include realization of the design that we proposed in Chapter 4, as this device can potentially dissipate high heat fluxes and be robust against pressure oscillations and modest contamination. It can also operate with higher interfacial temperature differences due to the higher mechanical strength. With the initial testing we did in [5], we demonstrated that the membrane supported on microchannels configuration (Figure 5-2) can dissipate high heat fluxes (>500 W/cm²) with low surface tension fluids such as pentane and R245fa, which we predicted to have higher evaporative heat transfer performance than water.

Figure 5-3 Schematic of a hydrophobic ultrathin nanoporous membrane that traps vapor between a high concentration solution and a low concentration solution. Evaporation and condensation occur through the nanopores between the two interfaces.
Further applications of the ultrathin nanoporous membrane may be fruitful in the field of water purification. For example, if we apply low surface energy coatings to the membrane, the structure is ideal for forward osmosis [103]. This concept is shown in Figure 5-3. Previously, we only investigated the case where the condenser is far away enough from the evaporator, so the gas flow eventually reaches thermodynamic equilibrium after enough intermolecular collisions. Fundamentally, with $L$ and $d$ (in Figure 5-3) smaller than the vapor mean free path, we can promote the ballistic molecular transport across the membrane to lower the overall transport resistance and yield ultrahigh vapor flux. More practically, when the lower concentration side contains other toxic substances, we can prepare a cleaner drawing solution (concentrated sugar or salt solution) to purify the water, which can be useful for emergency drinks and desalination.

Figure 5-4 (a) Schematic of evaporation through an ultrathin nanoporous membrane (unit cell) with heating and temperature sensing at the interface level. (b) Schematic of condensation through an ultrathin nanoporous membrane (unit cell) with temperature sensing at the interface and cooling flow underneath the membrane.
Additionally, if we reverse the temperature difference between the liquid and the vapor, the ultrathin nanoporous membrane may assist us in characterizing kinetically limited (ultrafast) condensation (Figure 5-4 a and b). At the interface level, it would be of great significance if we can compare the evaporation and condensation coefficients extracted from the experimental data and kinetic model to more conclusive non-equilibrium molecular dynamics studies that simulate the whole Knudsen layer, which is currently limited by the computing power. Overall, this thesis opened up quite a few opportunities of using the unique ultrathin nanoporous configuration.
Bibliography


